REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
26-11-2014

2. REPORT TYPE
Performance/Technical Report (Monthly)

3. DATES COVERED *(From - To)*
10/27/14 - 11/31/14

4. TITLE AND SUBTITLE
Polyfibroblast: A Self-Healing and Galvanic Protection Additive

5a. CONTRACT NUMBER

5b. GRANT NUMBER
N00014-09-1-0383

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER
FGY25

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
875 North Randolph Street
Arlington, VA 22203-1995

10. SPONSOR/MONITOR'S ACRONYM(S)
ONR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release: Distribution is Unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

15. SUBJECT TERMS
corrosion protection, self-healing, coatings, polymers

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
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					19b. TELEPHONE NUMBER *(Include area code)* 240-228-5140

REDD-2014-387

POLYFIBROBLAST PHASE IV: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #10

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Reporting Period: October 27, 2014 through November 31
Date of Report: November 26, 2014

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1 Summary

- A final report has been generated to describe the fundamental mechanisms that underpin the corrosion resistance of the self-healing paint. The manuscript shows that the synergistic effects of self-healing microcapsules combined with zinc powder create a greater improvement in damage tolerance than either by itself.
- A final report has been generated to describe the microencapsulation technology that was developed for the self-healing paint. The manuscript shows that our silica nanopowder-reinforced microcapsules have improved shelf life, solvent resistance, and mechanical properties relative to conventional polymer microcapsules.

2 Project Goals and Objectives

This final report will be accompanied by the submission of two manuscripts. Together, the two manuscripts summarize all of our accomplishments during phase I-IV of this program. They will hopefully lay the foundation for the development of the current self-healing paint technology, as well as future self-healing paint designs.

3 Key Accomplishments

3.1 Self-Healing Mechanisms Paper

Corrosion costs over $300 billion per year in the US, and as much as $4 billion per year to the Navy alone. The most cost effective method for preventing rust is to paint the surface. This protection, however, is only temporary, as paint inevitably develops scratches. The ability to make more durable coatings must be balanced against the convenience of spray painting. The latter effectively limits the feasible options to polymeric coatings, which, in turn, constrains the maximum achievable wear resistance. Rather than pursuing incremental improvements in *damage resistance* under these constraints, greater gains may be made through the development of *damage tolerant* coatings. To this end, we present a paint additive that confers self-healing

properties to commercial-off-the-shelf (COTS) primers. Used in conjunction with zinc-rich primers, it can prolong the lifetime of galvanic protection afforded by the sacrificial zinc.

Whether the self-healing agent in the microcapsule is able to protect the exposed surface from corrosion depends upon three steps: i) How long the agent takes to wet the exposed metal; ii) How long the agent takes to form an effective barrier layer; and iii) What happens to the surface before the first two steps complete. Under the right conditions, passivation of exposed steel delays the onset of corrosion for 6 weeks in a salt fog chamber, which compares to hours for a conventional paint and 1 week for a zinc-rich paint. Electrochemical impedance spectroscopy reveals how the mechanism of chemical passivation working in conjunction with cathodic protection is better than either strategy alone.

Control experiments showed that the octadecyltrimethoxy silane (OTS) corrosion inhibitor forms a passivation layer on both steel and zinc. In the case of steel, it blocks oxidants such as oxygen and water. In the case of zinc, it slows down the rate of oxidation. The situation in a three-layer CARC paint system is more complex. Moreover, galvanic protection is required in the initial stages following the scratch to preserve the freshly exposed steel long enough for self-healing to take place. Self-healing requires at least 48 hours to complete in most cases. OTS will not form an effective barrier layer if corrosion commences before its self-assembly completes. Once the OTS passivation layer has formed, however, it forms an insulating layer over the steel and zinc that allows the zinc to last much longer than it would in the absence of OTS-filled microcapsules.

3.2 Microcapsule Synthesis Paper

In the second paper, we report a one-pot synthesis for the production of Pickering microcapsules with outstanding strength, solvent resistance, and barrier properties. Octadecyltrimethoxysilane-filled (OTS) microcapsules form via standard interfacial polycondensation, except that silica nanopowder (10-20 nm diameter) replaces the conventional surfactant or hydrocolloid emulsifier. Isophorone diisocyanate (IPDI) in the OTS core reacts with diethylenetriamine, polyethylenimine, and water to form a hard polymer shell along the interface. Compared to pure polyurea, the silica-polyurea composite improves the shelf life of the OTS by about a factor of 10. The addition of SiO_2 prevents leaching of OTS into xylenes and hexanes for up to 80 days, and the resulting microcapsules survive nebulization through a spray gun at 620 kPa in a 500 cSt fluid.